

# Work functions of self-assembled monolayers on metal surfaces

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Using first-principles calculations we show that the work function of noble metals can be decreased or increased by up to 2 eV upon the adsorption of self-assembled monolayers of organic molecules. We identify the contributions to these changes for several (fluorinated) thiolate molecules adsorbed on Ag(111), Au(111) and Pt(111) surfaces. The work function of the clean metal surfaces increases in this order, but adsorption of the monolayers reverses the order completely. Bonds between the thiolate molecules and the metal surfaces generate an interface dipole, whose size is a function of the metal, but it is relatively independent of the molecules. The molecular and bond dipoles can then be added to determine the overall work function.

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Recent advances in molecular electronics, where organic molecules constitute active materials in electronic devices, have created a large interest in metal organic interfaces [1]. Transport of charge carriers across the interfaces between metal electrodes and the organic material often determines the performance of a device [2]. Organic semiconductors differ from inorganic ones as they are composed of molecules and intermolecular forces are relatively weak. In a bulk material this increases the importance of electron-phonon and electron-electron interactions [3]. At a metal organic interface the energy barrier for charge carrier injection into the organic material is often determined by the formation of an interface dipole localized at the first molecular layer. The interface dipole can be extracted by monitoring the change in the metal surface work function after deposition of an organic layer [1, 4].

Atoms and molecules that are physisorbed on a metal surface usually decrease the work function, as the Pauli repulsion between the molecular and surface electrons decreases the surface dipole [5, 6]. Chemisorption can give an increase or a decrease of the work function, and can even lead to counterintuitive results [7, 8]. Self-assembled monolayers (SAMs) are exemplary systems to study the effect of chemisorbed organic molecules upon metal work functions [9]. More specifically, alkyl thiolate ( $C_nH_{2n+1}S$ ) SAMs on the gold (111) surface are among the most extensively studied systems [10, 11, 12, 13, 14]. The sulphur atoms of the thiolate molecules form stable bonds to the gold surface and their alkyl tails are close packed, which results in a well ordered monolayer. SAMs with similar structures are formed by alkyl thiolates on a range of other (noble) metal surfaces [10, 14, 15].

Often the change in work function upon adsorption of a SAM is interpreted mainly in terms of the dipole moments of the individual thiolate molecules, whereas only a minor role is attributed to the change induced by chemisorption [9, 11, 12]. This assumption turns out to be reasonable for adsorption of methyl thiolate

( $CH_3S$ ) on Au(111) [13], but for  $CH_3S$  on Cu(111) it is not [14]. In this paper we apply first-principles calculations to study the interface dipoles and the work function change induced by adsorption of thiolate SAMs.

In particular, we analyze the contributions of chemisorption and of the molecular dipoles to uncover the effects of charge reordering at the interface. The chemical bonds between the thiolate molecules and the metal surfaces generate an interface dipole. We find that this dipole strongly depends upon the metal, but it is nearly independent of the electronegativity of the molecules. The size and direction of the interface dipole are such that it overcompensates for the difference between the clean metal work functions. This results in the SAM adsorbed on the highest work function metal having the lowest work function and vice versa. Modifying the molecular tails allows one to vary the absolute size of the work function over a range of more than 2 eV.

Since alkyl thiolate molecules form SAMs with a similar structure on (111) surfaces of several noble metals, they are ideal model systems for studying metal organic interfaces. By varying the relative electronegativity of surface and molecules one can induce electron transfer and create an interface dipole, without completely rearranging the interface structure. The electronegativity of a metal substrate is given by its work function. We consider the (111) surfaces of three metals that have a substantially different work function, but the same crystal structure and a similar lattice parameter: Ag (4.5 eV, 2.89 Å), Au (5.3 eV, 2.88 Å) and Pt (6.1 eV, 2.77 Å).

One would also like to vary the molecule's electronegativity without changing the structure of the SAM. This can be achieved by fluorinating the alkyl tails of thiolate molecules, which increases their electronegativity [10]. However, fluorinating the alkyl tails also reverses the polarity of the thiolate molecules and one has to separate this electrostatic effect from the charge reordering caused by chemisorption. In this paper we study the short chain thiolates  $CH_3S$ ,  $C_2H_5S$ ,  $CF_3S$ , and  $CF_3CH_2S$ .

Density functional theory (DFT) calculations are carried out using the projector augmented wave (PAW) method [16, 17], a plane wave basis set and the PW91 generalized gradient approximation (GGA) functional, as implemented in the VASP program [18, 19]. We use supercells containing a slab of at least five layers of metal atoms with a SAM adsorbed on one side of the slab and a vacuum region of  $\sim 12$  Å. The Brillouin zone of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  surface unit cell is sampled by a  $11 \times 11$   $\mathbf{k}$ -point grid. The plane wave kinetic energy cutoff is 450 eV. To avoid interactions between periodic images of the slab we apply a dipole correction [20]. The geometry of the SAM is optimized, as well as the positions of the top two layers of metal atoms. The atoms in the remaining metal layers are fixed at their bulk positions. The optimized bulk lattice parameters are 2.93, 2.94 and 2.79 Å for Ag, Au and Pt, respectively.

The work function is given by  $W = V(\infty) - E_F$ , where  $V(\infty)$  is the asymptotic electrostatic potential in vacuum, and  $E_F$  is the Fermi energy of the bulk metal.  $V(\infty)$  is extracted from the plane averaged potential  $\bar{V}(z) = A^{-1} \iint_A V(x, y, z) dx dy$ , with  $A$  the area of the surface unit cell. In practice,  $\bar{V}(z)$  reaches an asymptotic value within a distance of 5 Å from the surface. Accurate values of the Fermi energy are obtained following the procedure outlined in Ref. 21. By varying the computational parameters discussed above we estimate that the work functions are converged to within 0.05 eV. Typically DFT calculations give work functions that are within  $\sim 0.1$ - $0.2$  eV of the experimental values, although occasionally somewhat larger deviations are found.

The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure of  $\text{CH}_3\text{S}$  on  $\text{Au}(111)$  has been studied in several first-principles calculations [13, 14, 22, 23, 24]. We find basically the same optimized geometry as obtained in those calculations. Several structures exist that have a slightly different geometry, but are very close in energy, such as a  $c(4 \times 2)$  superstructure [23]. We find that the work functions of these structures are within 0.1 eV of that of the simpler structure, so we will not discuss these superstructures here.

The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure is also a good starting point for studying other systems. Thiolates with longer alkyl tails on  $\text{Au}(111)$  adopt this structure, as does  $\text{CH}_3\text{S}$  on  $\text{Pt}(111)$ , as well as alkyl thiolates on  $\text{Au}(111)$  whose end groups are fluorinated [10, 15]. Thiolates with long alkyl tails on  $\text{Ag}(111)$  form a somewhat denser packing, whereas long fluorinated alkyl thiolates form a somewhat less dense packing [10]. To analyze the work function we use optimized  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures for all our SAMs. We find that varying the packing density only introduces a scaling factor to the work function change [13].

Table I lists the calculated work functions. The work functions of the clean Au and Ag surfaces agree with the experimental values [25, 26], but that of Pt is  $\sim 0.3$  eV too low [27]. The latter can be attributed to the GGA functional. Using the local density approximation (LDA)

TABLE I: Calculated work functions  $W$  (eV) of clean (111) surfaces and of surfaces covered by SAMs in a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure.

	clean	$\text{CH}_3\text{S}$	$\text{C}_2\text{H}_5\text{S}$	$\text{CF}_3\text{S}$	$\text{CF}_3\text{CH}_2\text{S}$
Ag	4.50	3.95	4.13	6.14	6.30
Au	5.25	3.81	3.93	5.97	6.27
Pt	5.84(6.14 <sup>a</sup> )	3.45	3.47	5.68	5.87

<sup>a</sup>LDA value

the calculated work function of  $\text{Pt}(111)$  is 6.14 eV, which agrees with experiment. In other cases the difference between the work functions calculated with GGA and LDA functionals is much smaller. For instance, the GGA and LDA work functions of the SAMs on Pt are within 0.02 eV of one another. We will use the GGA values throughout this paper. The trend in the work functions of the SAM covered surfaces agrees well with experimental observations [9, 11, 12]. The experimental work function shifts with respect to the clean surface are sometimes somewhat smaller than the calculated ones [28].

The first observation one can make by comparing the numbers in Table I within columns is that on SAM covered surfaces the work function *decreases* in the order Ag, Au, Pt. This is striking, since the work function of the clean metal surfaces clearly *increases* in this order. Secondly, comparing the numbers within rows one finds that the work functions of the fluorinated alkyl thiolate covered surfaces are 2-2.5 eV higher than of the non-fluorinated ones. We will argue that the first observation can be ascribed to the interface dipole formed upon chemisorption. This interface dipole is independent of the molecular tails. The second observation will be interpreted in terms of the individual molecular dipoles.

In order to visualize the charge reordering at the surface upon adsorption of the SAM, we calculate the difference electron density  $\Delta n$ . It is obtained by subtracting from the total electron density  $n_{\text{tot}}$  of the SAM on the surface, the electron density  $n_{\text{surf}}$  of the clean surface and that of the free standing SAM  $n_{\text{SAM}}$ .  $n_{\text{surf}}$  and  $n_{\text{SAM}}$  are obtained in two separate calculations of a clean surface and a free standing SAM, respectively, with their structures frozen in the adsorbed geometry. As an example, Fig. 1 shows  $\Delta n$  for SAMs of  $\text{CF}_3\text{S}$  and  $\text{CH}_3\text{S}$  on  $\text{Ag}(111)$ .

Fig. 1 illustrates that  $\Delta n$  is localized mainly at the metal-SAM interface, i.e. near the sulphur atoms and the metal atoms in the first surface layers. In case of adsorption on Ag, electrons are transferred from the metal to the molecule, which results in an increase of the electron density on the sulphur atoms and a decrease on the surface metal atoms. The charge transfer does not depend strongly on the molecule, compare Figs. 1(a,b) to (c,d). This is somewhat surprising, since the electronegativity of  $\text{CF}_3\text{S}$  is much higher than that of  $\text{CH}_3\text{S}$ .

Very often a charge transfer between two systems is in-

TABLE II: Dipole per molecule  $\Delta\mu$ , from the change in work function upon adsorption. The (perpendicular) molecular dipole moment  $\mu_{\text{SAM}}$  in a free standing SAM. The chemisorption dipole moment is  $\mu_{\text{chem}} = \Delta\mu - \mu_{\text{SAM}}$ . All values are in D.

	Ag				Au				Pt			
	CH <sub>3</sub> S	C <sub>2</sub> H <sub>5</sub> S	CF <sub>3</sub> S	CF <sub>3</sub> CH <sub>2</sub> S	CH <sub>3</sub> S	C <sub>2</sub> H <sub>5</sub> S	CF <sub>3</sub> S	CF <sub>3</sub> CH <sub>2</sub> S	CH <sub>3</sub> S	C <sub>2</sub> H <sub>5</sub> S	CF <sub>3</sub> S	CF <sub>3</sub> CH <sub>2</sub> S
$\Delta\mu$	-0.32	-0.22	0.97	1.07	-0.86	-0.79	0.43	0.61	-1.28	-1.27	-0.08	0.02
$\mu_{\text{SAM}}$	-0.88	-0.79	0.44	0.50	-0.88	-0.81	0.44	0.53	-0.86	-0.80	0.37	0.47
$\mu_{\text{chem}}$	0.56	0.57	0.53	0.57	0.02	0.02	-0.01	0.08	-0.42	-0.47	-0.45	-0.45

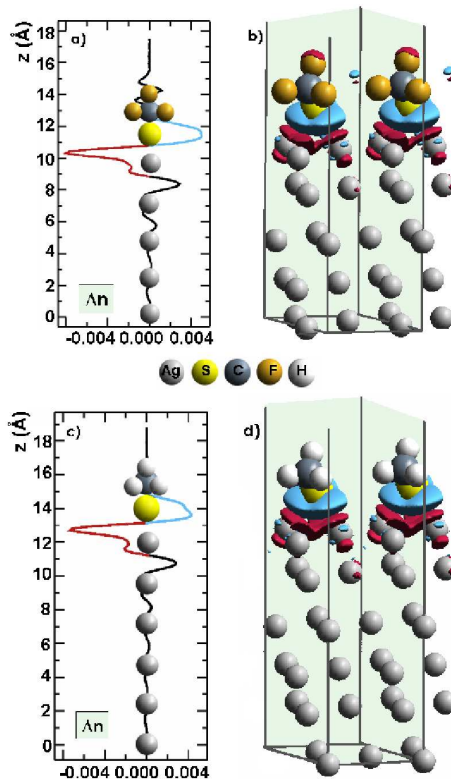


FIG. 1: (Color online) Difference electron density  $\Delta n = n_{\text{tot}} - n_{\text{surf}} - n_{\text{SAM}}$  for CF<sub>3</sub>S on Ag(111), (a) as function of  $z$ , averaged over the  $xy$  plane, in units of Å<sup>-3</sup>; (b) as an isodensity surface; (c), (d) the same for CH<sub>3</sub>S on Ag(111).

interpreted in terms of their relative electronegativity. For a metal surface the latter is simply the work function  $W_{\text{clean}}$ . For a molecule the Mulliken electronegativity  $\chi_M$  is defined as the average of the ionization potential and the electron affinity and considered to be the molecular equivalent of a chemical potential [29]. We find  $\chi_M = 5.4$  eV for the CH<sub>3</sub>S and CH<sub>3</sub>CH<sub>2</sub>S molecules. Since  $\chi_M$  is close to  $W_{\text{clean}}$  for Au(111), this would explain the lack of electron transfer upon adsorption of these molecules [13, 14]. However, the calculated  $\chi_M$  for CF<sub>3</sub>S and CF<sub>3</sub>CH<sub>2</sub>S are much higher, i.e. 6.9 eV and 6.1 eV, respectively. Yet this does not result in a markedly increased electron transfer to these molecules, as Fig. 1 indicates. It means that  $\chi_M$  is not a generally suitable parameter to predict the amount of charge transfer be-

tween surface and molecules.  $\chi_M$  reflects the relative stability of charged molecular states. In particular, for the thiolates  $\chi_M$  reflects the ability of the (fluorinated) alkyl chains to stabilize or screen charge that resides on the sulphur atom. We suggest that this is not important in case of adsorbed molecules, as the metal surface takes over this role.

Meanwhile, Fig. 1 suggests the following analysis. From the change in the work function upon adsorption of the SAM,  $\Delta W = W - W_{\text{clean}}$ , see Table I, one can obtain the change of the surface dipole upon adsorption,  $\Delta\mu = \epsilon_0 A \Delta W / e$  (with  $\epsilon_0$  the permittivity of vacuum and  $A$  the area of the surface unit cell). Since the unit cell contains one molecule,  $\Delta\mu$  is the change in the surface dipole per adsorbed molecule. The results are shown in Table II.  $\Delta\mu$  contains contributions from the charge re-ordering at the interface due to chemisorption, as well as from the dipole moments of the individual molecules.

The latter can be accounted for by calculating the dipole moment  $\mu_{\text{SAM}}$  per molecule of free standing SAMs, i.e. without the presence of a metal surface. We focus upon the component of the dipole that is perpendicular to the surface, since the other components do not contribute to the work function. As the calculation uses a full monolayer of molecules, it incorporates the effect on each molecule of the depolarizing field caused by the dipoles of all surrounding molecules. The calculated  $\mu_{\text{SAM}}$  are given in Table II. The structure of a SAM is fixed in its adsorption geometry, which is similar for the three metal surfaces. Therefore, the  $\mu_{\text{SAM}}$  values for adsorption on Ag, Au, and Pt in Table II differ only slightly. Of course  $\mu_{\text{SAM}}$  depends upon the molecule. In CH<sub>3</sub>S and CH<sub>3</sub>CH<sub>2</sub>S the dipole points from the sulphur atom to the alkyl group. The large electronegativity of fluor causes a reversal of the dipole in CF<sub>3</sub>S and CF<sub>3</sub>CH<sub>2</sub>S.

We define the contribution to the interface dipole resulting from chemisorption as  $\mu_{\text{chem}} = \Delta\mu - \mu_{\text{SAM}}$ . The results shown in Table II clearly demonstrate that  $\mu_{\text{chem}}$  is nearly independent of the molecule and strongly dependent on the metal substrate. As an independent check we have also calculated the dipole on the basis of the electron density redistribution, see Fig. 1,  $\mu_{\Delta n} = -e \iiint_{\text{cell}} z \Delta n(\mathbf{r}) dx dy dz$ . We find that  $\mu_{\Delta n} \approx \mu_{\text{chem}}$ , which indicates the consistency of this analysis.

The results obtained allow for a simple qualitative picture. The chemisorption dipole  $\mu_{\text{chem}}$  is very small for

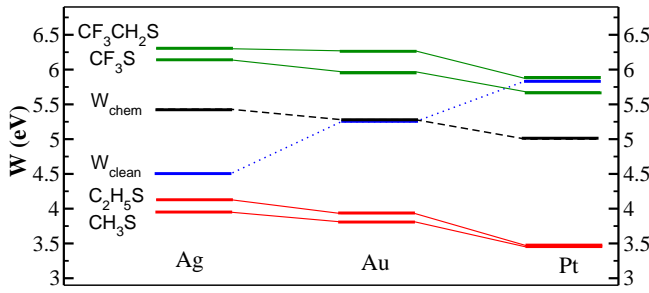


FIG. 2: (Color online) Work functions of clean surfaces  $W_{\text{clean}}$  (blue), including the chemisorption dipole  $W_{\text{chem}}$  (black), and of the SAM covered surfaces (red, green).

all SAMs on Au(111), indicating that the charge transfer between the Au surfaces and the molecules is small. This generalizes previous results obtained for methyl thiolate SAMs on Au(111) [13, 14]. Since the work function of Ag(111) is substantially lower than that of Au(111), a significant electron transfer takes place from the surface to the molecules for SAMs on Ag. This is confirmed by the values of  $\mu_{\text{chem}}$  for Ag in Table II. Fig. 1 shows that the electrons are transferred mainly to the sulphur atoms. Integrating the positive peak of  $\Delta n$  on the sulphur atom gives a charge of  $(-0.24 \pm 0.02)e$ . The sign of the charge transfer is such that  $\mu_{\text{chem}}$  increases the work function with respect to clean Ag(111). By a similar argument, since the work function of Pt(111) is much higher than that of Au(111), an electron transfer takes place from the molecules to the surface for adsorption on Pt. The values of  $\mu_{\text{chem}}$  for Pt in Table II confirm this. In this case the net charge on the sulphur atom is positive and  $\mu_{\text{chem}}$  decreases the work function with respect to clean Pt(111).

The size of the charge transfer is remarkable. Chemisorption creates an interface dipole  $\mu_{\text{chem}}$  that overcompensates for the difference between the metal work functions. We define a work function that includes the contribution from the chemisorption dipoles as  $W_{\text{chem}} = W_{\text{clean}} + e\mu_{\text{chem}}/(\epsilon_0 A)$ . The results shown in Fig. 2 demonstrate that  $W_{\text{chem}}$  decreases in the order Ag, Au and Pt, whereas  $W_{\text{clean}}$  increases in that order. The work function of the SAM covered surfaces can then be expressed as  $W = W_{\text{chem}} + e\mu_{\text{SAM}}/(\epsilon_0 A)$ . From the polarity of the molecules discussed above, it is clear that SAMs of  $\text{CH}_3\text{S}$  and  $\text{CH}_3\text{CH}_2\text{S}$  decrease the work function, whereas SAMs of  $\text{CF}_3\text{S}$  and  $\text{CF}_3\text{CH}_2\text{S}$  increase it.

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molecules with a larger polarizability are used, the effect of the depolarizing field of the molecular dipoles is larger, which reduces the interface dipole.

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